



A Weeks–Chandler–Andersen based potential fitting procedure for molecular dynamics simulations of the calcite–water interface



Sara Sjöblom^{*}, Bjørn Kvamme, Tatiana Kuznetsova

Department of Physics and Technology, University of Bergen, Allégaten 55, 5007 Bergen, Norway

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ABSTRACT

We propose a standardized potential fitting procedure capable of producing cross-term parameters required by classical molecular dynamic (MD) simulations of aqueous–mineral systems where pure species parameters for water, solutes and mineral are known. Unlike other approaches, our technique keeps the original pure-species partial charges intact and provides the short-range part of potential in cases when direct application of standard combination rules is not feasible. The procedure is based on Weeks–Chandler–Andersen potential splitting method with Barker–Henderson integration and yields effective hard-sphere diameter used as one of the fitting criteria. A set of water–calcite interaction parameters was produced and applied to model behaviour of water near $10\bar{1}4$ calcite surface by means of MD. The water structure was compared to both high-resolution XR data [1,2] and previous MD studies using various force fields [3–6]. Our simulations featuring fitted cross term parameters were found to be in general agreement with experimental data and proven more successful in matching water density profiles and ordering than previously utilized force field due to Hwang et al. [4,3].

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1. Introduction

Calcite is a naturally occurring form of calcium carbonate (CaCO_3) which is one of the most abundant minerals in the Earth's crust. It can be found in limestone deposits, coral reefs [7], skeletons, shells [8] and optical devices [9]. Depleted calcite dominated petroleum reservoirs can also be used for CO_2 sequestration [10]. Calcite has been the subject of extensive studies both on its own, as well as in interfacial systems with water, and more recently in more complex aqueous systems. From Yuen et al., in 1978 [11] who had one of the first force fields for CaCO_3 , to the work on shell models and rigid ion models of Pavese et al. [12,13], and Hwang et al.'s model based on the Dreiding force field [4,14], much work has been done to improve the models for bulk crystalline structure of CaCO_3 .

Atomistic studies of calcite then progressed to focus on calcite in contact with water. De Leeuw and Parker applied a core–shell model description to the calcite–water interfacial system [15,16], while Raiteri et al. proposed a rigid model description with both TIP4P–Ew [5,6] and SPC/Fw water [7,17]. Gale et al. derived a set of interaction parameters for reactive force-field approach [18]. In

their 2013 article, Fenter et al. [19] conducted a study comparing the agreement of molecular dynamic simulations with experimental x-ray data on the water–calcite interface. They concluded that while no force field succeeded in accurately matching the experimental findings, their own RIM models provided the overall best description of the interfacial water structure.

Recently, the challenge has shifted to aqueous systems containing calcite in contact with aqueous systems rather than pure water, where no cross term parameters exist to describe interaction between aqueous species and calcite. Different approaches have been proposed for finding the cross-interaction parameters, with the scarcity of experimental data, especially concerning measurable quantities which can be interpreted in terms of microscopic properties by MD, posing an additional challenge.

Freeman et al. [20] based their technique on existing potentials for the pure components and generated the missing cross terms relying on a methodology due to Schröder et al. [21]. This technique was applied in Freeman et al. [22] to molecular dynamic simulations of metanoic acid and methylamine in aqueous systems contacting calcite and magnesite surfaces. Cooke et al. [23] also used the approach of Freeman et al. [20] in their study of a calcite–water–ethanol system.

Nada [24] applied the approach to investigate the dynamics of aspartic acid (ASP) in the vicinity of different calcite cleaving

^{*} Corresponding author.

E-mail address: Sara.Sjoblom@uib.no (S. Sjöblom).

planes, using Lorentz-Berthelot mixing rules for the Lennard–Jones interaction between ASP and calcite oxygen and calcium. Neither Nada [24] nor Freeman et al. [22] papers performed any comparisons to experimental data.

The present work aimed to develop a transferable, standard procedure able to derive pair–pair interaction parameters for an aqueous calcite system containing solvent species where we lack specially fitted force field parameters for calcite–solvent interaction but have pure parameters available. The work was focused on investigating the details of water structuring near the 10 $\bar{1}4$ calcite surface and the effect of varying the parametrization parameters. The force fields under comparison included the force field due to Hwang et al. [4], a model used in our previous studies [3] with pure water parameters back-calculated to produce the cross terms of Hwang et al. [25], the RIM calcite–water potential of Raiteri et al. combined with the TIP4P-Ew water model [5], and calcite–water interatomic potential generated by the proposed scheme. Given the absence of any major surface restructuring of free calcite structures exposed to aqueous environment [5,26], we have fixed all calcite ions at their average crystallographic positions to allow for a longer time step of 1 fs.

In this paper, we investigate an approach with origins tracing to the equilibrium statistical mechanics of classical fluids [27,28] which aims to derive lacking cross interaction parameters directly from the pure species rather than fitted pair–pair force fields. The general methodology involved a modification of the van der Waals potential interaction rather than variation of partial charges. Instead of a straightforward application of Lorentz-Berthelot mixing rules, we devise a potential-fitting procedure based on Weeks–Chandler–Andersen (WCA) potential splitting, where Barker–Henderson-type integration is used to find the effective hard-sphere diameter. The goal of this paper is to apply our proposed procedure to derive interatomic potential parameters for water–calcite and test these parameters in extensive MD studies to compare the resulting water structuring in the vicinity of 10 $\bar{1}4$ calcite surface against experimental and simulation data.

2. Theoretical background

The idea of separating the repulsive and attractive forces in pair potentials is a well established approach. The short-range repulsive part, arising from overlapping electron shells, plays the decisive part in determining the structure of the liquid. Most of the liquid structure is contained in the interactions up to the potential minimum. The attractive part is considerably long range, and gives rise to an attractive background that helps stabilize the liquid [29]. Weeks, Chandler and Andersen (WCA) [27,28] suggested that for a classical fluid with pair interactions consisting of a short range harshly repulsive part and an attractive long range part, the Boltzmann factor for the short range harshly repulsive part is similar to that of hard-spheres. Weeks, Chandler and Andersen split the interaction potential into two parts at the minimum, $r = r_m$. One part, $r < r_m$, containing all repulsive forces, and the other part, $r > r_m$, containing all attractive forces. They then shifted the repulsive part upwards by the well depth ε :

$$\varphi^{\text{repulsive}}(r) = \begin{cases} \varphi(r) + \varepsilon & \text{for } r < r_m \\ 0 & \text{for } r \geq r_m \end{cases} \quad (1)$$

$$\varphi^{\text{attractive}}(r) = \begin{cases} -\varepsilon & \text{for } r < r_m \\ \varphi & \text{for } r \geq r_m \end{cases} \quad (2)$$

The steeper the repulsive part of the potential for $r < r_m$, the more it will resemble the hard-sphere potential:

$$\varphi(r) = \begin{cases} \infty & \text{for } r < d \\ 0 & \text{for } r \geq d \end{cases} \quad (3)$$

where d is the hard-sphere diameter [29,30]. The hard-sphere diameter can be found using the Barker–Henderson integration:

$$d = \int_0^\sigma (1 - e^{-\beta\varphi(z)}) dz \quad (4)$$

where d is the hard-sphere diameter, β the Boltzmann factor: $\beta = 1/(k_B T)$, φ the potential and $\varphi(\sigma) = 0$. This hard-sphere diameter will be a function of temperature, but independent of density [31]. In potential splitting due to Weeks, Chandler and Andersen, the short range part can be approximated by hard-spheres to the fourth order accuracy in Helmholtz free energy [28].

For our fitting procedure the Barker–Henderson hard-sphere diameter is calculated by

$$d = \int_0^{r_{\min}} (1 - e^{-(\varphi(z)+\varepsilon)/T}) dz \quad (5)$$

with the integral going to r_{\min} , and is shifted with ε since the WCA potential splitting was used.

2.1. Fitting procedure

The fitting program is a Fortran program which utilizes the effective hard-sphere diameter, the potential well depth, and the attractive-interaction integral (hereafter referred to as simply "area") as its fitting criteria inside the WCA potential splitting procedure with Barker–Henderson integration. The fitting procedure is outlined in the flow chart in Fig. 1.

The input consists of the pure parameters corresponding to species to be mixed (Lennard–Jones, Buckingham or a combination of the two types), the desired type of interatomic potential (Buckingham in our case), temperature, weight factors, and mixing option.

An iterative procedure is used to obtain the temperature-dependent hard-sphere diameter (d), potential well depth (ε) and area corresponding to both of the input species. If the input is Lennard–Jones in type, Barker–Henderson integration with a modified Romberg quadrature is applied to find the effective hard-sphere diameter. The Romberg method is a numerical technique based on the trapezoid rule [32]. The following integral is evaluated with the relative error set to 10^{-5} ; where ε/k_B is in Kelvin.

$$d = \int_0^{2^{1/6}\sigma} \left(1 - e^{-\left(4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right) + \varepsilon\right)/T}\right) dr \quad (6)$$

The well depth is equal to ε , and the area is found by performing Romberg integration with the relative error of 10^{-5} :

$$\text{area} = \int_\sigma^{3\sigma} 4\varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right) dr \quad (7)$$

If the input potential is of simplified Buckingham type, one must first determine the location of its minimum, r_{\min} , maximum, r_{\max} , and zero point, r_{zero} . The well depth will be equal to $\varphi(r_{\min})$. Romberg technique is once again applied to evaluate the integrals yielding the effective hard-sphere diameter and the area.

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